

## Application of the Finite-Element Method to the Hydrogen Atom in a Box in an Electric Field

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A better understanding of the problems of a pressurized atom and a crystal, both under the influence of a constant electric field, has been achieved through the numerical solution of the two-dimensional Schroedinger equation. The procedure consists of an adaptation of a finite-element package and gives fast and accurate results.

### INTRODUCTION

In a recent publication [1], it has been shown that the finite-element method could be applied for solving the two-dimensional Schroedinger equation. In the present work the method was used to treat the case of a hydrogen atom in a box in the presence of a constant external electric field.

The solution to this problem can be applied to investigate the atomic Stark effect and Stark ionization as well as the case of a Bloch electron in an electric field. Although the atomic Stark effect and ionization is quite an old problem [2, 3], it has been constantly under investigation [4]. Our aim was to examine this problem for a pressurized system. To that end we used a simple model, namely, the finite box. The application of this model to the atomic problem has already been proposed by Michels *et al.* [5], and to the crystal problem—by Wigner and Huntington [6]. Recently, there has been a renewed interest in the box model [7-9]. The case of a free electron in a box with an applied electric field was treated as an "empty crystal

problem" [10] and also by the Green's function method [11] where the density of states for the high levels was obtained.

The crystal and the atomic cases differ over boundary conditions imposed on the boxes' faces. We used two types of boundary conditions:

(a) The wavefunction vanishes (a Dirichlet problem)—this is an approximation for a pressurized atom.

(b) The normal derivative of the wavefunction vanishes (a Neumann problem)—this provides an approximation for a crystal under pressure.

We solved both cases for various spherical boxes. Using the finite-element technique [12]. Since an external electric field was present, we had to consider separately different magnetic quantum numbers. When the quantum number did not vanish, this technique had to be carefully used so that one could by-pass a nonconvergence phenomena. The procedure is given in detail in the next section, followed by the numerical results and discussion.

#### THE NUMERICAL METHOD

The stationary Schroedinger equation for a single particle of mass  $m_0$ , moving in the potential field  $V(r)$ , is

$$-\frac{\hbar^2}{2m_0} \nabla^2 \psi(r) + V(r) \psi(r) = E \psi(r), \quad (1)$$

where  $r \equiv (x, y, z)$ ,  $E$  is a possible energy level, and  $\psi$  is the corresponding wavefunction.

Using the units of I for a hydrogen atom with no electric field one obtains the equation

$$y \nabla^2 \phi + \frac{\partial \phi}{\partial y} + \left( \frac{2y}{\rho} + \epsilon y \right) \phi = 0, \quad (2)$$

where  $y = r \sin \theta$ ,  $x = r \cos \theta$  and  $\rho^2 = x^2 + y^2$ . The complete study of Eq. (2) was already given in I.

In this work two more terms were added to Eq. (2), namely,  $-m^2/y$  and  $\eta xy$ , to form the more general equation:

$$y \nabla^2 \phi + \frac{\partial \phi}{\partial y} + \left( \frac{2y}{\rho} - \frac{m^2}{y} + \eta xy + \epsilon y \right) \phi = 0 \quad (3)$$

where  $m (= 0, 1, 2, \dots)$  is the magnetic quantum number and  $\eta$  represents the external electric field, which is in the  $x$ -direction.  $\eta$  has the form:

$$\eta = \frac{2\hbar^4}{m_0^2 e^5} E. \quad (4)$$

If the units of  $E$  are V/cm, then  $\eta = 1.869 \times 10^{-9}E$ . For  $\eta \neq 0$  the potential is no longer spherically symmetric and the energy levels for different values of  $m$  are not the same. The domain of solution was

$$D \triangleq \{(x, y) \mid x^2 + y^2 \leq R^2, y \geq 0\} \quad (5)$$

and the boundary conditions are

$$\phi(x, y) = 0, \quad x^2 + y^2 = R^2 \quad (6a)$$

for our Dirichlet problem, and

$$\frac{\partial \phi}{\partial n}(x, y) = 0, \quad x^2 + y^2 \leq R^2 \quad (6b)$$

for a Neumann problem. If  $m \neq 0$ , an additional boundary condition, namely,

$$\phi(x, 0) = 0, \quad |x| \leq R \quad (7)$$

is needed so that the term  $-m^2/y$  in Eq. (3) would not lead to a singularity. When substituting  $y = 0$  into Eq. (3) for the  $m = 0$  case, one sees that a natural boundary condition exists, which is

$$\frac{\partial \phi}{\partial n}(x, 0) = 0, \quad |x| \leq R \quad (\text{for } m = 0). \quad (8)$$

Throughout the numerical work the term  $-m^2/y$  was integrated over a triangular element such that one of its sides was with

$$L \triangleq \{(x, 0) \mid 0 \leq x \leq R\} \quad (9)$$

Evidently, the double integral  $\iint (m^2/y) dx dy$  over such an element does not converge near  $y = 0$ . However, the eigenvalues of Eq. (3) should not be affected by this region  $\tau$ , since its contribution depends on the expression (e.g., perturbation theory)  $\iint |\phi|^2 (m^2/y^2) d\tau$  and we know (by substitution) that  $\phi/y$  is bounded when  $y \rightarrow 0$ . In order to check whether our numerical device could handle these singularities we ran the following tests: (a) The eigenvalues for  $m \neq 0$ ,  $\eta = 0$  were compared with those for  $m = 0$ . [1]. The difference, as a rule, was on the order of  $10^{-4}$ . (b) The domain of integration was taken to be

$$D^* \triangleq \{(x, y) \mid x^2 + y^2 \leq R^2, y \geq \delta\} \quad (10)$$

and we let  $\delta$  approach zero. The eigenvalues hardly changed.

Another approach avoiding the calculation of the singular integral is to define a new eigenfunction  $\psi$  by

$$y^\alpha \psi(x, y) = \phi(x, y). \quad (11)$$

Substituting  $\psi$  in Eq. (3) one obtains

$$y^{2\alpha+1}\nabla^2\psi + (1 + 2\alpha)y^{2\alpha}\frac{\partial\psi}{\partial y} + y^{2\alpha-1}\left(\alpha^2 - m^2 + \frac{2y^2}{\rho} + \eta xy^2 + \epsilon y^2\right)\psi = 0 \quad (12)$$

with

$$\psi(x, 0) = 0, \quad m^2 \neq \alpha^2, \quad (13a)$$

$$\frac{\partial\psi}{\partial n}(x, 0) = 0, \quad m^2 = \alpha^2 \quad (13b)$$

as necessary boundary conditions.

TABLE I

The energy levels  $\epsilon$ , calculated for  $m = 1, \alpha = 0, \frac{1}{2}, R = 2$ .

|                        |       |       |        |        |        |        |        |        |
|------------------------|-------|-------|--------|--------|--------|--------|--------|--------|
| $\alpha = 0$           | 3.153 | 6.656 | 10.757 | 12.737 | 15.558 | 20.689 | 20.936 | 26.856 |
| $\alpha = \frac{1}{2}$ | 3.173 | 6.666 | 10.707 | 12.617 | 15.439 | 19.673 | 20.863 | 26.879 |

TABLE II

The energy levels  $\epsilon$  for  $R = 2, 0 \leq m \leq 3$ ; a Dirichlet problem

| $l$ | $m = 0$<br>(Ref. [1]) | $m = 1$ | $m = 2$ | $m = 3$ |
|-----|-----------------------|---------|---------|---------|
| 0   | -0.250                |         |         |         |
| 1   | 3.153                 | 3.153   |         |         |
| 2   | 6.656                 | 6.656   | 6.656   |         |
| 0   | 6.661                 |         |         |         |
| 3   | 10.761                | 10.759  | 10.756  | 10.755  |
| 1   | 12.780                | 12.776  |         |         |
| 4   | 15.562                | 15.558  | 15.550  | 15.541  |
| 2   | 20.670                | 20.689  | 20.688  |         |
| 0   | 20.759                |         |         |         |
| 5   | 20.940                | 20.936  | 20.929  | 20.917  |
| 6   | 26.848                | 26.856  | 26.837  | 26.819  |
| 3   | 27.791                | 27.787  | 27.784  | 27.774  |
| 1   | 32.289                | 32.285  |         |         |
| 7   | 33.365                | 33.422  | 33.345  | 33.310  |
| 4   | 35.285                | 35.288  | 35.168  | 35.051  |

There is now no singularity as long as  $\alpha > 0$ . Although the eigenvalues for a fixed value of  $m$  should be the same for all  $\alpha$  the numerical accuracy decreases for  $\alpha > 0$  (Table 1). This could be explained in the following manner: Eq. (3) is elliptic over  $D$  except for  $y = 0$ , where it becomes parabolic. Transformation (11) for  $\alpha > 0$  causes the coefficient of  $\nabla^2\psi$  to be of a higher power of  $y$  ( $= y^{2\alpha+1}$ ). One should then expect greater trouble near  $y = 0$  in solving Eq. (12) rather than Eq. (3), since the transition to parabolicity is more pronounced.

Hence, this approach was not adopted and direct integration of Eq. (3) was used.

### THE ENERGY LEVELS

We solved Eqs. (3), (6a) and Eqs. (3), (6b), for  $R = 0.5, 2, 5.02, 6; 0 \leq \eta \leq 100$  and  $m = 0, 1, 2, 3$ . Table II shows the equivalence of the eigenvalues for different magnetic quantum numbers and  $\eta = 0$ . Figure 1 describes the potential in the presence of an electric field ( $\eta \neq 0$ ), as a function of  $x$  for  $y = 0$ . Except for the bound electrons whose wavefunctions are obviously prominent for region I, one gets energy levels for electrons which are predominantly in region III, especially for high fields and large radii. These electrons are distinguished by their wavefunctions being concentrated

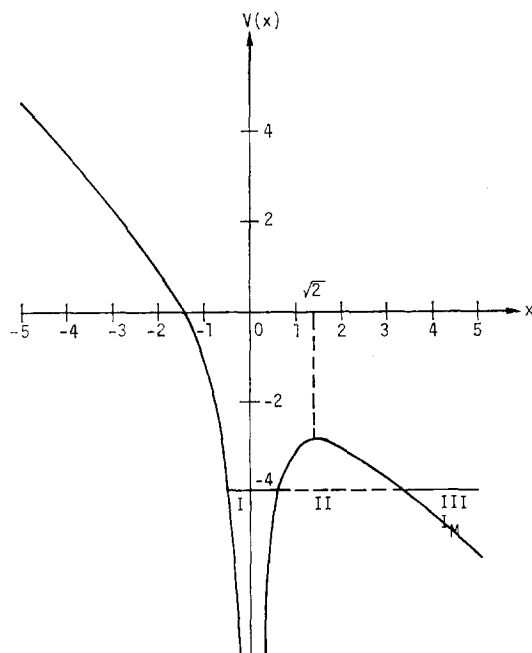


FIG. 1. The potential  $V(x)$  seen by the electron along the  $y = 0$  plane ( $R = S$ ).  $V(x) = 2/|x| + \eta x$ , where the first term describes the atomic influence, and the second is the potential of the constant electric field (applied along the  $x$ -axis).

TABLE III

Wavefunction concentration near  $r = R$ ,  $R = 5.02$ ,  $\eta = 10$ ,  $m = 0$ ,  $\epsilon_1 = -44$ .

| $x$          | 0      | 1.255 | 2.510 | 3.765 | 5.020 |
|--------------|--------|-------|-------|-------|-------|
| $\phi(x, 0)$ | -0.005 | 0.02  | -0.02 | 0.11  | 0.73  |

near  $x = R$ . Table III shows an example of this phenomenon, consisting of the wavefunction's values along the  $x$ -axis for  $R = 5.02$ ,  $\eta = 10$ ,  $m = 0$ , and for the first energy level.

Tables IV and V show the first energy levels for  $m = 0$  and  $m = 1$ , respectively, for a Dirichlet problem,  $R = 2$ , and for various values of  $\eta$  within the range  $0 \leq \eta \leq 100$ .

TABLE IV

The energy levels  $\epsilon$ ,  $R = 2$ ,  $m = 0$ ,  $0 \leq \eta < 100$ ; a Dirichlet problem

| $\eta = 0$ | 0.1    | 0.3    | 1      | 2      | 3      | 4      | 5      | 10     | 100      |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|----------|
| -0.250     | -0.250 | -0.257 | -0.335 | -0.589 | -1.005 | -1.566 | -2.253 | -6.907 | -138.046 |
| 3.153      | 3.152  | 3.146  | 3.083  | 2.893  | 2.620  | 2.294  | 1.929  | -0.563 | -114.500 |
| 6.657      | 6.657  | 6.653  | 6.605  | 6.449  | 6.199  | 5.867  | 5.464  | 2.768  | -89.196  |
| 6.660      | 6.660  | 6.663  | 6.704  | 6.817  | 6.954  | 7.068  | 7.127  | 6.244  | -88.207  |
| 10.766     | 10.766 | 10.766 | 10.765 | 10.758 | 10.731 | 10.666 | 10.551 | 9.201  | -62.401  |
| 12.782     | 12.782 | 12.782 | 12.782 | 12.783 | 12.792 | 12.812 | 12.841 | 12.689 | -58.283  |
| 15.561     | 15.561 | 15.561 | 15.560 | 15.554 | 15.547 | 15.537 | 15.525 | 15.335 | -35.161  |
| 20.488     | 20.488 | 20.485 | 20.459 | 20.372 | 20.233 | 20.050 | 19.831 | 18.449 | -33.848  |

TABLE V

The energy levels  $\epsilon$ ,  $R = 2$ ,  $m = 1$ ,  $0 \leq \eta < 100$ ; a Dirichlet problem

| $\eta = 0$ | 0.1    | 1      | 2      | 10     | 100      |
|------------|--------|--------|--------|--------|----------|
| 3.153      | 3.152  | 3.073  | 2.840  | -2.628 | -125.311 |
| 6.657      | 6.656  | 6.632  | 6.557  | 3.770  | -100.627 |
| 10.762     | 10.762 | 10.757 | 10.738 | 8.993  | -75.407  |
| 12.771     | 12.771 | 12.754 | 12.704 | 11.094 | -71.577  |
| 15.558     | 15.558 | 15.555 | 15.547 | 14.953 | -48.690  |
| 20.490     | 20.489 | 20.464 | 20.388 | 18.726 | -36.325  |
| 20.950     | 20.950 | 20.949 | 20.948 | 20.900 | -21.194  |
| 26.955     | 26.955 | 26.957 | 26.963 | 26.744 | -9.946   |

The Dirichlet and the Neumann problems differ in the rate of change of the eigenvalues with  $\eta$ . The influence of the external electric field is stronger for the Neumann case and for larger  $R$ 's. This behavior is expected since the contribution of the field term to the eigenvalue is proportional to  $\int x |\phi|^2 dx$ , which depends upon the charge distribution of the wavefunction. The latter is more concentrated at small  $x$  for the Dirichlet problem [10] and causes the decreasing of the above integral. Table VI shows the differences in  $\epsilon$  between  $\eta = 0$  and  $\eta = 10$ , namely,  $\epsilon(\eta = 10) - \epsilon(\eta = 0)$ , for both Dirichlet and Neumann cases and for  $R = 0.5, 2, 5.02$ . The calculated values are denoted by  $\Delta\epsilon_0^{10}(D)$  and  $\Delta\epsilon_0^{10}(N)$  respectively, and the first eight differences for each problem are considered.

The behavior of the energy levels as  $R$  increases is shown in Table VII. The first five energy levels for a Neumann problem are given for  $0.5 \leq R \leq 6$  and  $\eta = 0$ . These levels describe the bottom end of the energy bands obtained for the Wigner-Seitz crystal and are in agreement with previous results [13].

TABLE VI

Changes in energy levels in the presence of an external electric field and  $m = 0$ 

| $\Delta\epsilon_0^{10}(D)$ | $R = 0.5$                  |                            | $R = 2$                    |                            | $R = 5.02$                 |  |
|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|----------------------------|--|
|                            | $\Delta\epsilon_0^{10}(N)$ | $\Delta\epsilon_0^{10}(D)$ | $\Delta\epsilon_0^{10}(N)$ | $\Delta\epsilon_0^{10}(D)$ | $\Delta\epsilon_0^{10}(N)$ |  |
| -1.260                     | -0.263                     | -6.657                     | -12.661                    | -35.776                    | -42.991                    |  |
| -0.183                     | 0.091                      | -3.710                     | -7.607                     | -31.854                    | -39.470                    |  |
| -0.032                     | 0.033                      | -3.889                     | -4.583                     | -26.600                    | -35.255                    |  |
| -0.207                     | -0.021                     | -0.416                     | -3.651                     | -25.223                    | -31.365                    |  |
| 0.020                      | 0.019                      | -1.565                     | -1.144                     | -21.941                    | -26.835                    |  |
| 0.060                      | 0.014                      | -0.093                     | -2.391                     | -20.031                    | -26.774                    |  |
| -0.007                     | -0.004                     | 0.226                      | 1.614                      | -17.065                    | -22.544                    |  |
| 0.013                      | 0.011                      | -2.000                     | -1.607                     | -13.655                    | -22.108                    |  |

TABLE VII

Energy levels for a Neumann problem;  $\eta = 0, 0.5 \leq R \leq 6$ .

| $R$ | $\epsilon_1$ | $\epsilon_2$ | $\epsilon_3$ | $\epsilon_4$ | $\epsilon_5$ |
|-----|--------------|--------------|--------------|--------------|--------------|
| 0.5 | -6.110       | 12.064       | 39.716       | 69.716       | 76.720       |
| 1   | -3.123       | 1.689        | 8.684        | 14.318       | 17.978       |
| 2   | -1.659       | -0.250       | 1.546        | 2.029        | 3.892        |
| 3   | -1.218       | -0.416       | 0.202        | 0.407        | 1.462        |
| 4   | -1.057       | -0.410       | -0.249       | 0.071        | 0.671        |
| 5   | -1.007       | -0.378       | -0.351       | -0.057       | 0.332        |
| 6   | -0.990       | -0.355       | -0.346       | -0.111       | 0.163        |

## STARK EFFECT

For small values of the electric field (i.e., for small  $\eta$ ), the energy levels should behave according to the well-known theory [14] of the Stark effect. This effect is calculated by the perturbation method, and the boundary conditions of the present work evidently do not change the following qualitative conclusions (Table VIII): (a) For well-separated energy levels the effect is of second order, i.e.,  $\Delta\epsilon \propto \eta^2$  for small  $\eta$  (induced dipole moment). (b) For degenerate levels, the effect is linear, i.e.,  $\Delta\epsilon \propto \eta$ , for small  $\eta$  (permanent dipole moment). This result is also obtained approximately for closely spaced levels. Table VIII demonstrates the Stark effect for the well-separated level  $\epsilon_1$  and for the closely spaced levels  $\epsilon_2, \epsilon_3$ , for  $m = 0$ . Similar behavior occurs for Dirichlet problems, as well.

TABLE VIII

The Stark effect for a Neumann Problem,  $R = 6, m = 0$

| $\eta$ | $\epsilon_1$ | $\epsilon_2$ | $\epsilon_3$ |
|--------|--------------|--------------|--------------|
| 0      | -0.99024     | -0.35536     | -0.34638     |
| 0.01   | -0.99037     | -0.37668     | -0.32753     |
| 0.02   | -0.99079     | -0.40391     | -0.30783     |

## IONIZATION

Our model can be used to calculate the ionization probability for the low-lying hydrogenic excited levels. Ionization is viewed as a tunneling process by which a bound electron passes from region I to region III (Fig. 1). Evidently tunneling should be approached carefully since we have calculated steady-state solutions. Tunneling calculations are usually carried out for one-dimensional problems. The case of the infinite box (free-atom ionization) can be brought to a one-dimensional form by using parabolic coordinates [3, 4]. In our case, however, the procedure is invalid because of the spherical boundary conditions. We use a one-dimensional method devised for treating multidimensional tunneling problems [15, 16]. In this method a path minimizing the action integral is sought and the tunneling probability is calculated along this path. We calculated the ionization probability [14] for the  $m = 0$  case and for Neumann boundary conditions. The extension of the method to other conditions is obvious. For  $m = 0$  the least action path is along the  $x$ -axis (see Fig. 1). The expression for the ionization probability is

$$S = \frac{\exp\{-2 \int_{II} (1 - 2/\rho + \eta x - \epsilon)^{1/2} dx\}}{4 \int_I (-2/\rho + \eta x - \epsilon)^{-1/2} dx}, \quad (14)$$



TABLE IX

Ionization probability for Neumann problems,  $R = 5.02$ ,  $m = 0$ 

| $\eta$ | $\epsilon_2$ | $\ln S$ |
|--------|--------------|---------|
| 0.0100 | -0.389       | -40.3   |
| 0.0125 | -0.394       | -29.2   |
| 0.0150 | -0.399       | -21.7   |
| 0.0175 | -0.404       | -15.8   |
| 0.0200 | -0.409       | -10.1   |

where the normalization was carried out along region I (i.e., inside the atom). Values of  $\ln S$  are given in Table IX, for the first excited energy levels.

All the computations were carried out on the CDC CYBER-73 computer of the Ben Gurion University. The average computing time needed for a complete solution (i.e., calculation of the energy levels for either a Dirichlet or a Neumann problem) was 2.5 min.

#### CONCLUSIONS

A finite element approach has been proposed for solving two-dimensional Schrodinger equations. Its efficiency, applicability, and accuracy were demonstrated with examples—a pressurized hydrogen atom and a crystal in the presence of a constant electric field. The same system in the presence of a magnetic field is now being studied.

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